

APPENDIX G

**STATISTICAL AND GEOCHEMICAL EVALUATIONS
OF SITE METALS DATA**

STATISTICAL

Statistical Comparison of Site and Background Data For Former Rifle/Machine Gun Range, Parcel 104Q Fort McClellan, Alabama

1.0 Introduction

This report provides the Tier 1 and Tier 2 (Shaw E&I, 2003) site-to-background comparison results for Former Rifle/Machine Gun Range, Parcel 104Q, Fort McClellan, in Calhoun County, Alabama. In the first step of the comparison, the maximum detected concentration (MDC) of each element is compared to two times the arithmetic mean of the background data (SAIC, 1998). Any metal that has an MDC greater than the background screening value is carried forward for Tier 2 evaluation, which includes the Slippage Test and the Wilcoxon Rank Sum Test (WRS). If either or both of these statistical test cannot be done, the evaluation will include the Hot Measurement Test.

The methodology and results of the Tier 1 and Tier 2 comparisons are summarized in Tables 1 through 3, and described in more detail in the following sections. Site samples used in the site-to-background comparison include 22 surface soil samples (0 to 1 foot below ground surface [bgs]), 22 total soil (0 to 4 feet bgs), and 2 groundwater samples that were collected at the site.

Background distributions and screening values have been established for target analyte list metals in surface soil, total soil (surface and subsurface soil combined), and groundwater for Fort McClellan (SAIC, 1998).

2.0 Comparison Methodology

This section describes the statistical techniques that were employed in Parcel 104Q statistical site-to-background comparison.

2.1 Statistical Procedures

Contamination can be caused by a variety of processes that yield different spatial distributions of elevated contaminant concentrations. Slight but pervasive contamination can occur from non-point-source releases, and can result in slight increases in contaminant concentrations in a large percentage of samples. Localized, or “hot-spot,” contamination can result in elevated concentrations in a small percentage of the total number of site samples. No single two-sample statistical comparison test is sensitive to both of these modes of contamination. For this reason, the use of several simultaneous tests is recommended for a valid and complete comparison of site

Table 1

**Summary of Tier 1 and Tier 2 Site to Background Comparison for Surface Soil
Former Rifle/Machine Gun Range, Parcel 104Q
Fort McClellan, Calhoun County, Alabama**

Metals	Frequency of Detection	Tier 1 Evaluation ^a	Tier 2 Evaluation			Carried Forward for Tier 3 Geochemical Evaluation
			Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	
Aluminum	22 / 22	Failed	Passed	Failed	NA	Yes
Antimony	0 / 22	NA	NA	NA	NA	
Arsenic	22 / 22	Passed	NA	NA	NA	
Barium	22 / 22	Failed	Passed	Failed	NA	Yes
Beryllium	12 / 22	Passed	NA	NA	NA	
Cadmium	0 / 22	NA	NA	NA	NA	
Calcium	22 / 22	Passed	NA	NA	NA	
Chromium	22 / 22	Failed	Passed	Passed	NA	
Cobalt	22 / 22	Passed	NA	NA	NA	
Copper	22 / 22	Failed	Passed	Passed	NA	
Iron	22 / 22	Passed	NA	NA	NA	
Lead	22 / 22	Failed	Passed	Failed	NA	Yes
Magnesium	22 / 22	Passed	NA	NA	NA	
Manganese	22 / 22	Failed	Passed	Failed	NA	Yes
Mercury	20 / 22	Failed	Passed	NA ^d	Failed	Yes
Nickel	21 / 22	Failed	Passed	Failed	NA	Yes
Potassium	14 / 22	Passed	NA	NA	NA	
Selenium	0 / 22	NA	NA	NA	NA	
Silver	0 / 22	NA	NA	NA	NA	
Sodium	19 / 22	Passed	NA	NA	NA	
Thallium	0 / 22	NA	NA	NA	NA	
Vanadium	22 / 22	Passed	NA	NA	NA	
Zinc	22 / 22	Passed	NA	NA	NA	

NA = not applicable

a Tier 1 evaluation per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or Wilcoxon Rank Sum (WRS) test cannot be performed.

d WRS test is not performed on data sets containing 50% or more nondetects.

Table 2

**Summary of Tier 1 and Tier 2 Site to Background Comparison for Total Soil
Former Rifle/Machine Gun Range, Parcel 104Q
Fort McClellan, Calhoun County, Alabama**

Metals	Frequency of Detection	Tier 1 Evaluation ^a	Tier 2 Evaluation			Carried Forward for Tier 3 Geochemical Evaluation
			Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	
Aluminum	44 / 44	Failed	Passed	Failed	NA	Yes
Antimony	0 / 44	NA	NA	NA	NA	
Arsenic	44 / 44	Passed	NA	NA	NA	
Barium	44 / 44	Passed	NA	NA	NA	
Beryllium	23 / 44	Failed	Passed	Failed	NA	Yes
Cadmium	0 / 44	NA	NA	NA	NA	
Calcium	44 / 44	Failed	Passed	Failed	NA	Yes
Chromium	44 / 44	Failed	Passed	Passed	NA	
Cobalt	43 / 44	Passed	NA	NA	NA	
Copper	44 / 44	Failed	Passed	Passed	NA	
Iron	44 / 44	Passed	NA	NA	NA	
Lead	44 / 44	Failed	Passed	Failed	NA	Yes
Magnesium	44 / 44	Passed	NA	NA	NA	
Manganese	44 / 44	Failed	Passed	Failed	NA	Yes
Mercury	39 / 44	Failed	Passed	Failed	NA	Yes
Nickel	43 / 44	Passed	NA	NA	NA	
Potassium	29 / 44	Passed	NA	NA	NA	
Selenium	0 / 44	NA	NA	NA	NA	
Silver	0 / 44	NA	NA	NA	NA	
Sodium	40 / 44	Passed	NA	NA	NA	
Thallium	0 / 44	NA	NA	NA	NA	
Vanadium	44 / 44	Failed	Passed	Passed	NA	
Zinc	44 / 44	Passed	NA	NA	NA	

NA = not applicable

a Tier 1 evaluation per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or Wilcoxon Rank Sum (WRS) test cannot be performed.

Table 3

**Summary of Tier 1 and Tier 2 Site to Background Comparison for Groundwater
Former Rifle/Machine Gun Range, Parcel 104Q
Fort McClellan, Calhoun County, Alabama**

Metals	Frequency of Detection	Tier 1 Evaluation ^a	Tier 2 Evaluation			Carried Forward for Tier 3 Geochemical Evaluation
			Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	
Aluminum	0 / 2	NA	NA	NA	NA	
Antimony	0 / 2	NA	NA	NA	NA	
Arsenic	0 / 2	NA	NA	NA	NA	
Barium	2 / 2	Passed	NA	NA	NA	
Beryllium	0 / 2	NA	NA	NA	NA	
Cadmium	0 / 2	NA	NA	NA	NA	
Calcium	2 / 2	Passed	NA	NA	NA	
Chromium	0 / 2	NA	NA	NA	NA	
Cobalt	0 / 2	NA	NA	NA	NA	
Copper	0 / 2	NA	NA	NA	NA	
Iron	1 / 2	Passed	NA	NA	NA	
Lead	0 / 2	NA	NA	NA	NA	
Magnesium	2 / 2	Passed	NA	NA	NA	
Manganese	2 / 2	Passed	NA	NA	NA	
Mercury	0 / 2	NA	NA	NA	NA	
Nickel	0 / 2	NA	NA	NA	NA	
Potassium	1 / 2	Passed	NA	NA	NA	
Selenium	0 / 2	NA	NA	NA	NA	
Silver	0 / 2	NA	NA	NA	NA	
Sodium	0 / 2	NA	NA	NA	NA	
Thallium	0 / 2	NA	NA	NA	NA	
Vanadium	0 / 2	NA	NA	NA	NA	
Zinc	0 / 2	NA	NA	NA	NA	

NA = not applicable

a Tier 1 evaluation per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or Wilcoxon Rank Sum (WRS) test cannot be performed.

versus background distributions (U.S. Environmental Protection Agency [EPA], 1989, 1992, and 1994; U.S. Navy, 2002).

Analytes that fail the Tier 1 and Tier 2 comparisons are subject to a geochemical evaluation to determine if the elevated concentrations are due to natural processes or if they represent potential contamination.

2.1.1 Tier 1

In this step of the background screening process, the MDC of the site data set is compared to the background screening value of two times the background mean (SAIC, 1998). Elements for which the site MDC does not exceed the background screening value are considered to be present at background concentrations, and are not considered site-related chemicals. Elements for which the site MDC exceeds the background screening value undergo further evaluation (Tier 2).

2.1.2 Tier 2

Slippage Test. The nonparametric Slippage test is designed to detect a difference between the upper tails of two distributions, and has been recommended for use in site-to-background comparisons to identify potential localized, or hot-spot, contamination (U.S. Navy, 2002). The test is performed by counting the number (K) of detected concentrations in the site data set that exceed the maximum background measurement, and then comparing this number to a critical value (K_c), which is a function of the number of background samples and the number of site samples. If $K > K_c$, then potential contamination is indicated and the analyte will be subjected to geochemical evaluation. If $K \leq K_c$, then localized contamination is not suspected.

Critical values tables for site and background data sets up to size $n = 50$ are provided in U.S. Navy (2002). Critical values for larger data sets are calculated using the test statistic provided in Rosenbaum (1954). In this report, the Slippage test is performed at the 95 percent confidence level. The test cannot be performed if the maximum background value is a nondetect, because the actual concentration in that sample is unknown.

Wilcoxon Rank Sum Test. The nonparametric WRS test is designed to detect a difference between the medians of two data sets, and has been recommended for use in site-to-background comparisons to identify slight but pervasive contamination (EPA, 2000; U.S. Navy, 2002). In this report, the WRS test is performed when the site and background data sets each contain less than 50 percent nondetects (i.e., measurements reported as not detected below the laboratory

reporting limit). The WRS test will not be performed on data sets containing 50 percent or more nondetects. The medians of such data sets are unknown, and hence the test results would lack sufficient power to yield reliable results.

The WRS test compares two data sets of size n and m ($n > m$), and tests the null hypothesis that the samples were drawn from populations with distributions having the same medians. To perform the test, the two sets of observations are pooled and arranged in order from smallest to largest. Each observation is assigned a rank; that is, the smallest is ranked 1, the next largest is ranked 2, and so on up to the largest observation, which is ranked $(n + m)$. If ties occur between or within samples, each one is assigned the mid-rank. Next, the sum of the ranks of smaller data set m is calculated. Then the test statistic Z is determined,

$$Z = \frac{W - m(m + n + 1)/2}{\sqrt{mn(m + n + 1)/12}}$$

Where:

W = Sum of the ranks of the smaller data set

m = Number of data points in smaller group

n = Number of data points in larger group.

This test statistic Z is used to find the two-sided significance. For instance, if the test statistic yields a probability of a Type I error (p-level) less than 0.2, then there is a statistically significant difference between the medians at the 80 percent confidence level. A Type I error involves rejecting the null hypothesis when it is true. If the p-level is greater than 0.2, then there is no reasonable justification to reject the null hypothesis at the 80 percent confidence level. It can therefore be concluded that the medians of the two data sets are similar, and it can be assumed to be drawn from the same population.

If the p-level is less than 0.2, then the medians of the two distributions are significantly different at the 80 percent confidence level. This can occur if the site data are shifted higher or lower than the background data. If the site data are shifted higher relative to background, then contamination may be indicated, and the analyte in question will be carried on for geochemical evaluation; however, if the site data are shifted lower relative to background, then contamination is not indicated. If the p-level is greater than 0.2, then pervasive site contamination is not suspected.

Box Plots. A quick, robust graphical method recommended by the EPA to visualize and compare two or more groups of data is the box plot comparison (EPA, 1989 and 1992). These plots provide a summary view of the entire data set, including the overall location and degree of symmetry. The box encloses the central 50 percent of the data points so that the top of the box represents the 75th percentile and the bottom of the box represents the 25th percentile. The small box within the larger box represents the median of the data set. The upper whisker extends outward from the box to the maximum point and the lower whisker extends to the minimum point. Nondetect results are set equal to one-half of the reporting limit for plotting purposes.

For each analyte, box plots of site and background data are placed side by side to visually compare the distributions and qualitatively determine whether the data sets are similar or distinct. Accordingly, the box plots are a necessary adjunct to the WRS test. As described previously, the WRS test may indicate that the medians of the site and background data sets are significantly different. Examination of the box plots will confirm whether that difference is caused by site data that are shifted higher or lower relative to background.

Hot Measurement Test. The hot measurement test consists of comparing each site measurement with a concentration value that is representative of the upper limit of the background distribution (EPA, 1994). Ideally, a site sample with a concentration above the background screening value would have a low probability of being a member of the background distribution, and may be an indicator of contamination. It is important to select such a background screening value carefully so that the probability of falsely identifying site samples as contaminated or uncontaminated is minimized.

The 95th upper tolerance limit (95th UTL) is recommended as a screening value for normally or lognormally distributed analytes and the 95th percentile is recommended as a screening value for nonparametrically distributed analytes (EPA, 1989, 1992, and 1994). Site samples with concentrations above these values are not necessarily contaminated, but should be considered suspect. To perform the test, each analyte's site MDC is compared to the background 95th UTL or 95th percentile, in accordance with the type of background distribution. If the site MDC exceeds the background screening value, then that analyte will undergo a geochemical evaluation. If the MDC does not exceed the background threshold value, then hot-spot contamination is not indicated.

2.1.3 Geochemical Evaluation

If an analyte fails either of the statistical tests described above, then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The methodology and results of the geochemical evaluation are provided in Appendix H.

3.0 Results of the Site-to-Background Comparisons

This section presents the results of the site-to-background comparisons for 23 TAL metals in Parcel 104Q surface soil, total soil, and groundwater samples. Tables 1 through 3 summarize the Tier 1 and Tier 2 test results for each media as discussed in the following sections. Statistical test results are discussed in detail below. Box plots are also discussed below and are provided in Attachment 1.

3.1 Surface Soil

Twenty-three TAL metals were evaluated in Parcel 104Q surface soil. Five metals (antimony, cadmium, selenium, silver, and thallium) had no detected concentrations in surface soil. No further discussion of these metals is included.

Ten metals (arsenic, beryllium, calcium, cobalt, iron, magnesium, potassium, sodium, vanadium, and zinc) had no detected concentrations above the background screening value, passing the Tier 1 evaluation. These metals are considered within the range of background and will not be tested or discussed any further.

The remaining 8 metals underwent Tier 2 evaluation. The statistical test results and box plots are discussed in detail below.

Table 1 summarizes the Tier 1 and Tier 2 test results for surface soil.

Aluminum

Tier 1 Evaluation

Six site samples exceed the background screening value of 16,306 milligrams per kilogram (mg/kg).

Slippage Test

The critical value, K_c , for aluminum is 3. Aluminum has no site samples exceeding the maximum background measurement ($K=0$). Because $K < K_c$, aluminum passes the Slippage test.

WRS Test

The WRS test p-level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

Box plots for the site and background data sets are provided in Figure 1-1. The site minimum and interquartile range are higher than the corresponding background values. The site maximum is less than that of background.

Conclusion

Because aluminum in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Barium

Tier 1 Evaluation

Three site samples exceed the background screening value of 123.94 mg/kg.

Slippage Test

K_c for barium is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, barium passes the Slippage test.

WRS Test

The p-level of 0.00296 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-1). The site maximum is less than background.

Conclusion

Because barium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Chromium

Tier 1 Evaluation

One site sample exceeds the background screening value of 37.04 mg/kg.

Slippage Test

K_c for chromium is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, chromium passes the Slippage test.

WRS Test

The p-level of 0.15 indicates weak agreement between the site and background distributions.

Box Plot

The site median, 75th percentile, and maximum are less than the corresponding background values (Figure 1-2). The site minimum is slightly higher than the corresponding background value, and the site and background 25th percentiles are the same.

Conclusion

Because chromium in surface soil passes the Tier 2 evaluation, it is considered to be within the range of background.

Copper

Tier 1 Evaluation

Two site samples exceed the background screening value of 12.71 mg/kg.

Slippage Test

K_c for copper is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, copper passes the Slippage test.

WRS Test

The p-level of 0.8 indicates excellent agreement between the site and background distributions.

Box Plot

The site and background medians are similar (Figure 1-2). The site minimum and 25th percentile are higher than that of background, and the site 75th percentile and maximum are lower than that of background.

Conclusion

Copper in surface soil is considered to be within the range of background.

Lead

Tier 1 Evaluation

Two site samples exceed the background screening value of 40.05 mg/kg.

Slippage Test

K_c for lead is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, lead passes the Slippage test.

WRS Test

The p-level of 0.07 indicates weak agreement between the site and background distributions.

Box Plot

The site minimum, 25th percentile, median, and 75th percentile are higher than the corresponding background values (Figure 1-3). The site maximum is less than that of background.

Conclusion

Because lead in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Manganese

Tier 1 Evaluation

Five site samples exceed the background screening value of 1,579 mg/kg.

Slippage Test

The critical value, K_c , for manganese is 3. No detects in site samples exceed the maximum background measurement. Because $K < K_c$, manganese passes the Slippage test.

WRS Test

The p-level of 0.0127 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than their respective background values (Figure 1-3). The site maximum is lower than that of background.

Conclusion

Because manganese in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Mercury

Tier 1 Evaluation

Six site samples exceed the background screening value of 0.08 mg/kg.

Slippage Test

K_c for mercury is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, mercury passes the Slippage test.

WRS Test

The WRS test was not performed because the background data set has more than 50 percent nondetects.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-4). The site maximum is less than that of background. The shape and location of the background box plot are influenced by the percentage of nondetects (66 percent), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC exceeds the background 95th percentile of 0.125 mg/kg.

Conclusion

Because mercury in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Nickel

Tier 1 Evaluation

One site sample exceeds the background screening value of 10.33 mg/kg.

Slippage Test

K_c for nickel is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, nickel passes the Slippage test.

WRS Test

The p-level of 0.04 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-4). The site maximum is less than that of background.

Conclusion

Because nickel in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

3.2 Total Soil

Twenty-three TAL metals were evaluated in Parcel 104Q total soil. Five metals (antimony, cadmium, selenium, silver, and thallium) had no detected concentrations. No further discussion of these metals is included.

Nine metals (arsenic, barium, cobalt, iron, magnesium, nickel, potassium, sodium, and zinc) had no detected concentrations above the background screening value, passing the Tier 1 evaluation these metals are considered within the range of background. No further testing or discussion of these metals is included.

The remaining 9 metals underwent Tier 2 evaluation. The statistical tests and box plots are discussed in detail below.

Table 2 summarizes the Tier 1 and Tier 2 test results for total soil.

Aluminum

Tier 1 Evaluation

Twenty-four site samples exceed the background screening value of 15,009 mg/kg.

Slippage Test

The critical value, K_c , for aluminum is 3. No site samples exceed the maximum background measurement. Because $K < K_c$, aluminum passes the Slippage test.

WRS Test

The p-level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-5). The site maximum is less than that of background.

Conclusion

Because aluminum in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Beryllium

Tier 1 Evaluation

One site sample exceeds the background screening value of 0.831 mg/kg.

Slippage Test

K_c for beryllium is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, beryllium passes the Slippage test.

WRS Test

The p-level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, 25th percentile, and median are higher than the corresponding background values (Figure 1-5). The site 75th percentile is similar to that of background, and the site maximum is lower than that of background.

Conclusion

Because beryllium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Calcium

Tier 1 Evaluation

One site sample exceeds the background screening value of 1,204.25 mg/kg.

Slippage Test

K_c for calcium is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, calcium passes the Slippage test.

WRS Test

The p-level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, 25th percentile, and median are lower than the corresponding background range (Figure 1-6). The site and background 75th percentiles are the same, and the site maximum is lower than that of background.

Conclusion

Because calcium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Chromium

Tier 1 Evaluation

One site sample exceeds the background screening value of 37.623 mg/kg.

Slippage Test

K_c for chromium is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, chromium passes the Slippage test.

WRS Test

The p-level of 0.032 indicates a significant difference between the site and background distributions. The box plot shows the difference to be that the site data is less than the background.

Box Plot

The site interquartile range and maximum are lower than the corresponding background range (Figure 1-6). The site minimum is greater than that of background.

Conclusion

Chromium in total soil is considered to be within the range of background.

Copper

Tier 1 Evaluation

One site sample exceeds the background screening value of 15.93 mg/kg.

Slippage Test

K_c for copper is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, copper passes the Slippage test.

WRS Test

The p-level of 0.36 indicates a good agreement between the site and background distributions.

Box Plot

The site median is slightly lower than that of background (Figure 1-7). The site minimum and 25th percentile are higher than the corresponding background values, and the site 75th percentile and maximum are lower than that of background.

Conclusion

Copper in total soil passes the Tier 2 evaluation and is considered to be within the range of background.

Lead

Tier 1 Evaluation

Two site samples exceed the background screening value of 39.324 mg/kg.

Slippage Test

K_c for lead is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, lead passes the Slippage test.

WRS Test

The p-level of 0.0386 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, 25th percentile, and median are higher than the corresponding background values (Figure 1-7). The site 75th percentile appears to be the same as background, and the site maximum is lower than that of background.

Conclusion

Because lead in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Manganese

Tier 1 Evaluation

Seven site samples exceed the background screening value of 1,472 mg/kg.

Slippage Test

K_c for manganese is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, manganese passes the Slippage test.

WRS Test

The p-level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum is significantly higher than that of background, and the site interquartile range is slightly higher than the corresponding background range (Figure 1-8). The site maximum is less than that of background.

Conclusion

Because manganese in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Mercury

Tier 1 Evaluation

Twenty site samples exceed the background screening value of 0.0704 mg/kg.

Slippage Test

K_c for mercury is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, mercury passes the Slippage test.

WRS Test

The WRS test was not performed because the background data set has more than 50 percent nondetects.

Box Plot

The site minimum and interquartile range are higher than that of the corresponding background values (Figure 1-8). The site maximum is slightly less than that of background. The shape and location of the background box plot are influenced by the percentage of nondetects (60 percent), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC exceeds the background 95th percentile of 0.094 mg/kg.

Conclusion

Because mercury in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Vanadium

Tier 1 Evaluation

One site sample exceeds the background screening value of 61.7 mg/kg.

Slippage Test

K_c for vanadium is 3, and no site samples exceed the maximum background measurement. Because $K < K_c$, vanadium passes the Slippage test.

WRS Test

The p-level of 0.616 indicates a strong agreement between the site and background distributions.

Box Plot

The site median is slightly lower than that of background (Figure 1-9). The site minimum and 25th percentile are slightly higher than the corresponding background values, and the site 75th percentile and maximum are lower than background.

Conclusion

Vanadium in total soil passed the Tier 2 evaluation and is considered to be within the range of background.

3.3 Groundwater

This section presents the results of the site-to-background comparisons for 23 metals in unfiltered groundwater samples.

Seventeen metals (aluminum, antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, silver, sodium, thallium, vanadium, and zinc) had no detected results in the site samples and are not discussed any further.

The remaining six metals (barium, calcium, iron, magnesium, manganese, and potassium) had no detected concentrations that exceeded their respective background screening value. These metals passed the Tier 1 evaluation and are considered to be within the range of background. They will not be included in any further evaluation or discussion.

4.0 Summary and Conclusions

The statistical methodology used to compare site data from the Former Rifle/Machine Gun Range, Parcel 104Q and the background data for 23 elements in surface soil, total soil, and groundwater, includes a comparison of the site MDC to the background screening value (Tier 1 evaluation). Analytes that failed this comparison were subjected to the Slippage test and Wilcoxon rank sum test, and box-and-whisker plots were prepared to visually compare the two data sets and properly interpret the WRS test results. If the Slippage test and/or the WRS test could not be performed, the Hot Measurement test was included as part of the Tier 2 statistical evaluation. Analytes that underwent Tier 2 evaluation and failed any component of the statistical site-to-background comparison are carried forward for Tier 3 geochemical evaluation to determine if natural processes can explain the elevated concentrations.

Tables 1 through 3 summarize the comparison test results and the metals carried forward for geochemical evaluation.

5.0 References

Rosenbaum, S., 1954, "Tables for a Nonparametric Test of Location," *Annals of Mathematical Statistics*, Vol. 24, pp. 146-150.

Science Application International Corporation (SAIC), 1998, *Final Background Metals Survey Report, Fort McClellan, Anniston, Alabama*, prepared for U.S. Army Corps of Engineers, Mobile, Alabama, July.

Shaw Environmental and Infrastructure (Shaw E&I), 2003, ***Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2***, Technical Memorandum, 24 June 2003 by Paul Goetchius.

U.S. Environmental Protection Agency (EPA), 1989, ***Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Interim Final Guidance***, Office of Solid Waste, Waste Management Division, EPA/530/SW-89/026, July.

U.S. Environmental Protection Agency (EPA), 1992, ***Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance***, Environmental Statistics and Information Division, Office of Policy, Planning, and Evaluation, EPA/530/R-93/003, July.

U.S. Environmental Protection Agency (EPA), 1994, ***Statistical Methods For Evaluating The Attainment Of Cleanup Standards***, Environmental Statistics and Information Division, Office of Policy, Planning, and Evaluation, EPA/230/R-94/004, June.

U.S. Environmental Protection Agency (EPA), 2000, ***Guidance for Data Quality Assessment: Practical Methods for Data Analysis, EPA QA/G-9, QA00 Update***, Office of Environmental Information, EPA/600/R-96/084, July.

U.S. Navy, 2002, ***Guidance for Environmental Background Analysis, Volume 1: Soil***, NFESC User's Guide UG-2049-ENV, Naval Facilities Engineering Command, Washington, D.C., April.

ATTACHMENT 1

Figure 1-1

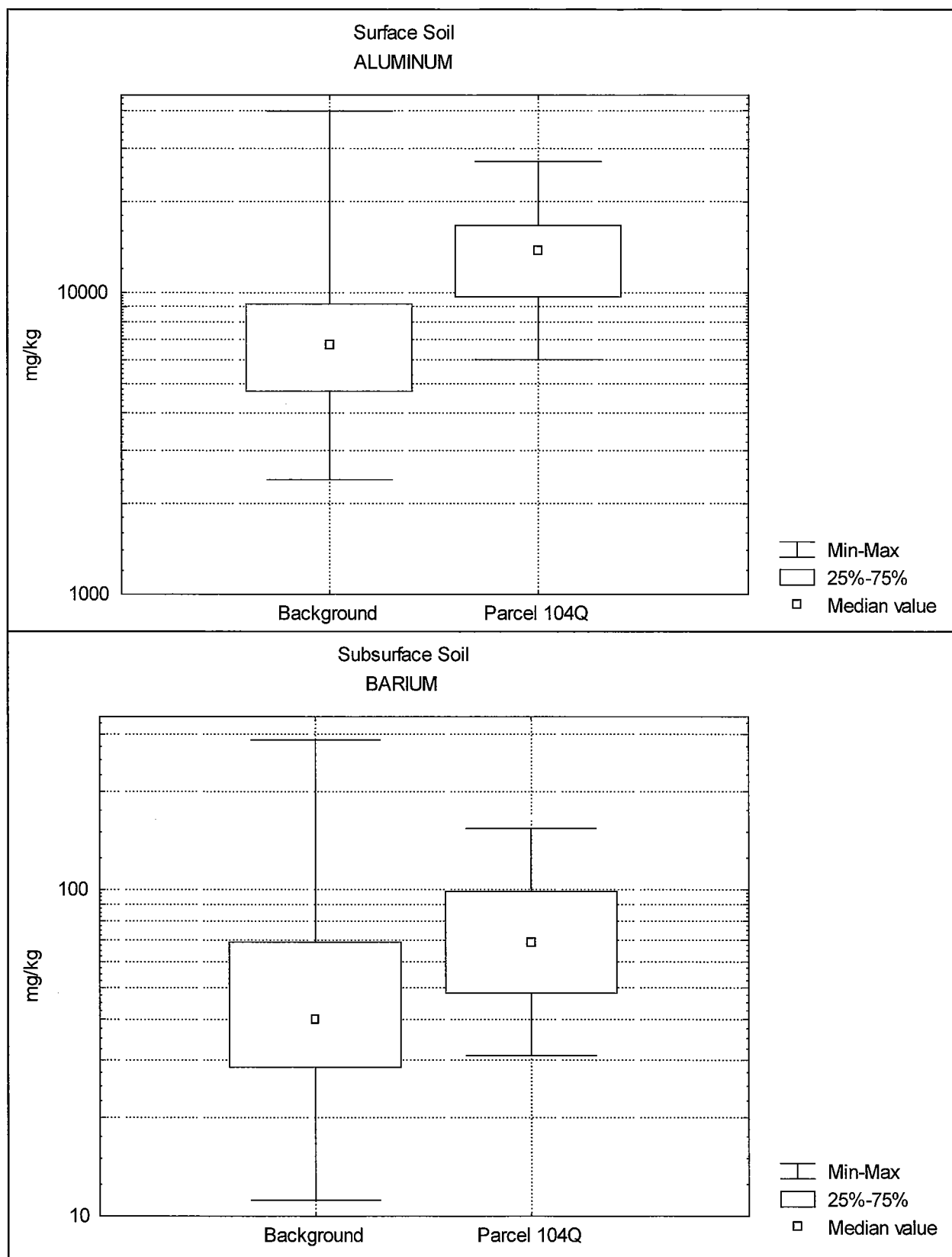


Figure 1-2

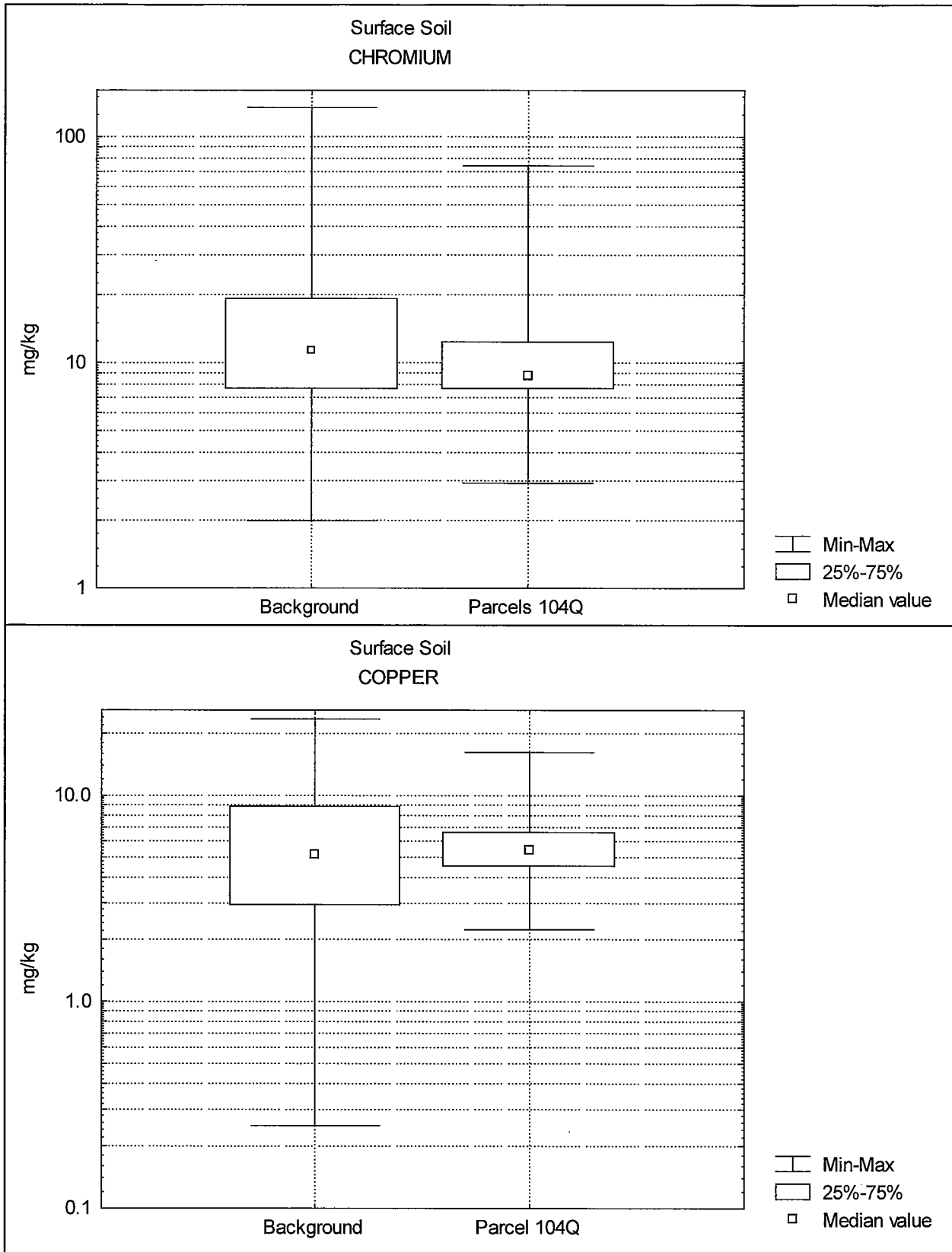


Figure 1-3

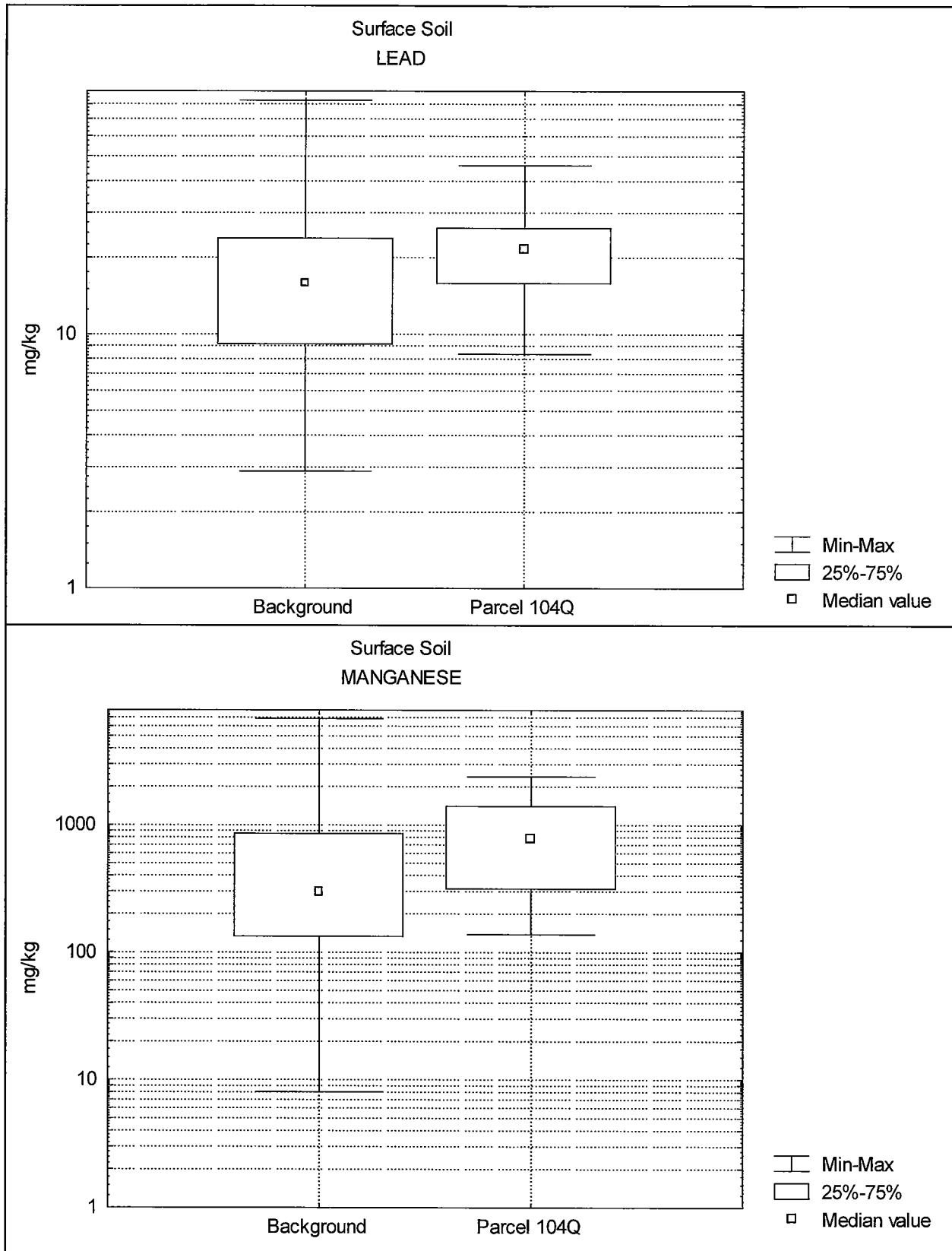


Figure 1-4

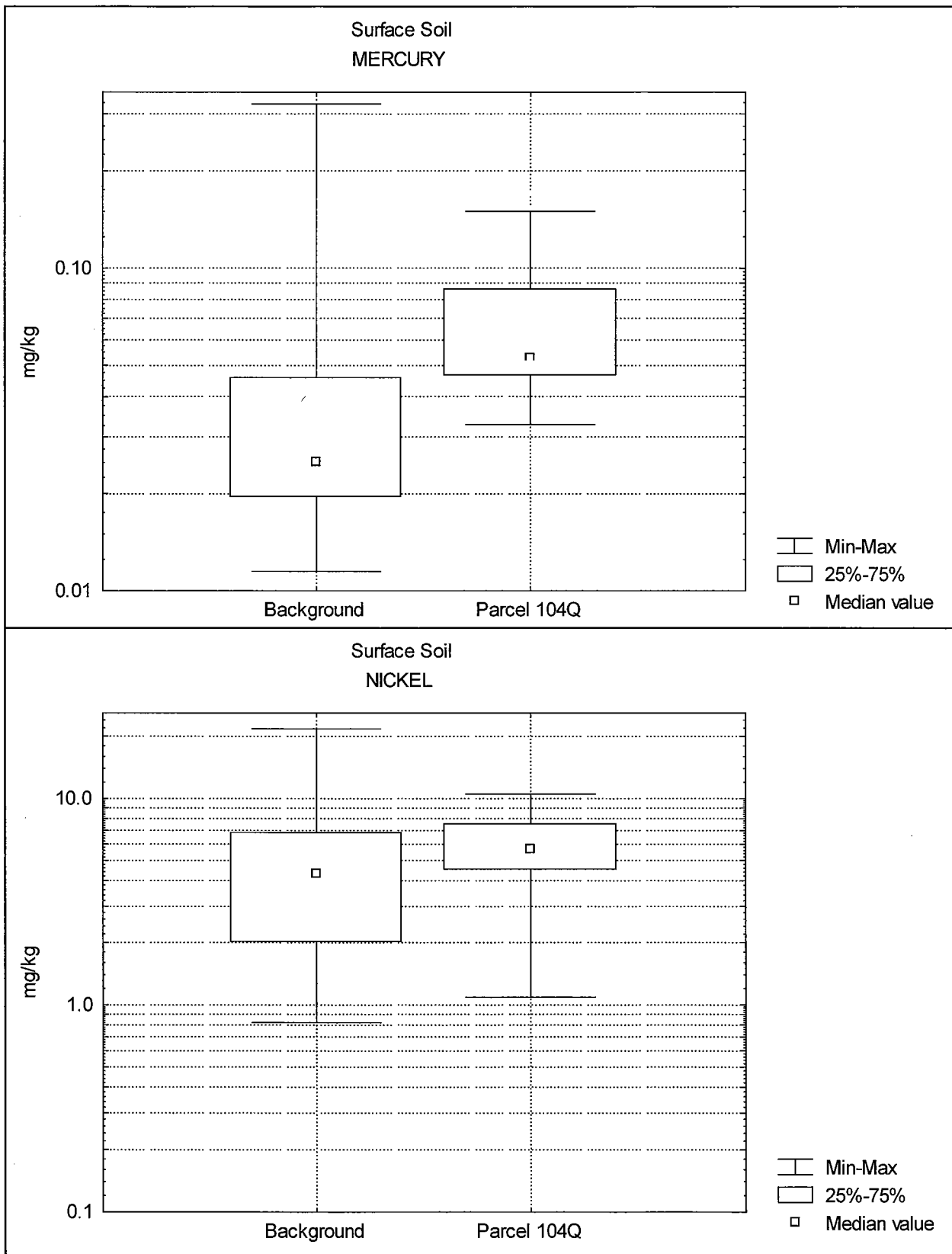


Figure 1-5

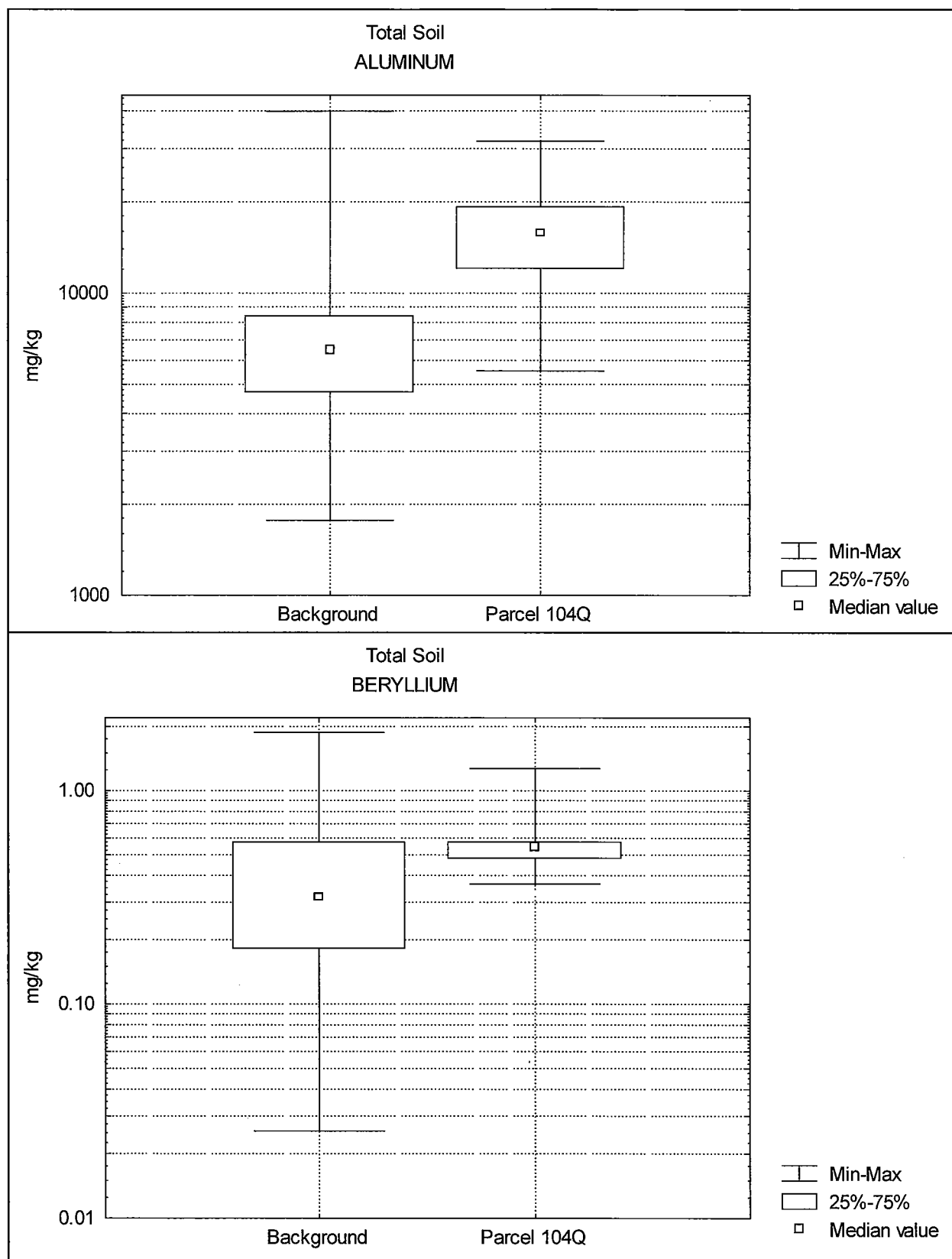


Figure 1-6

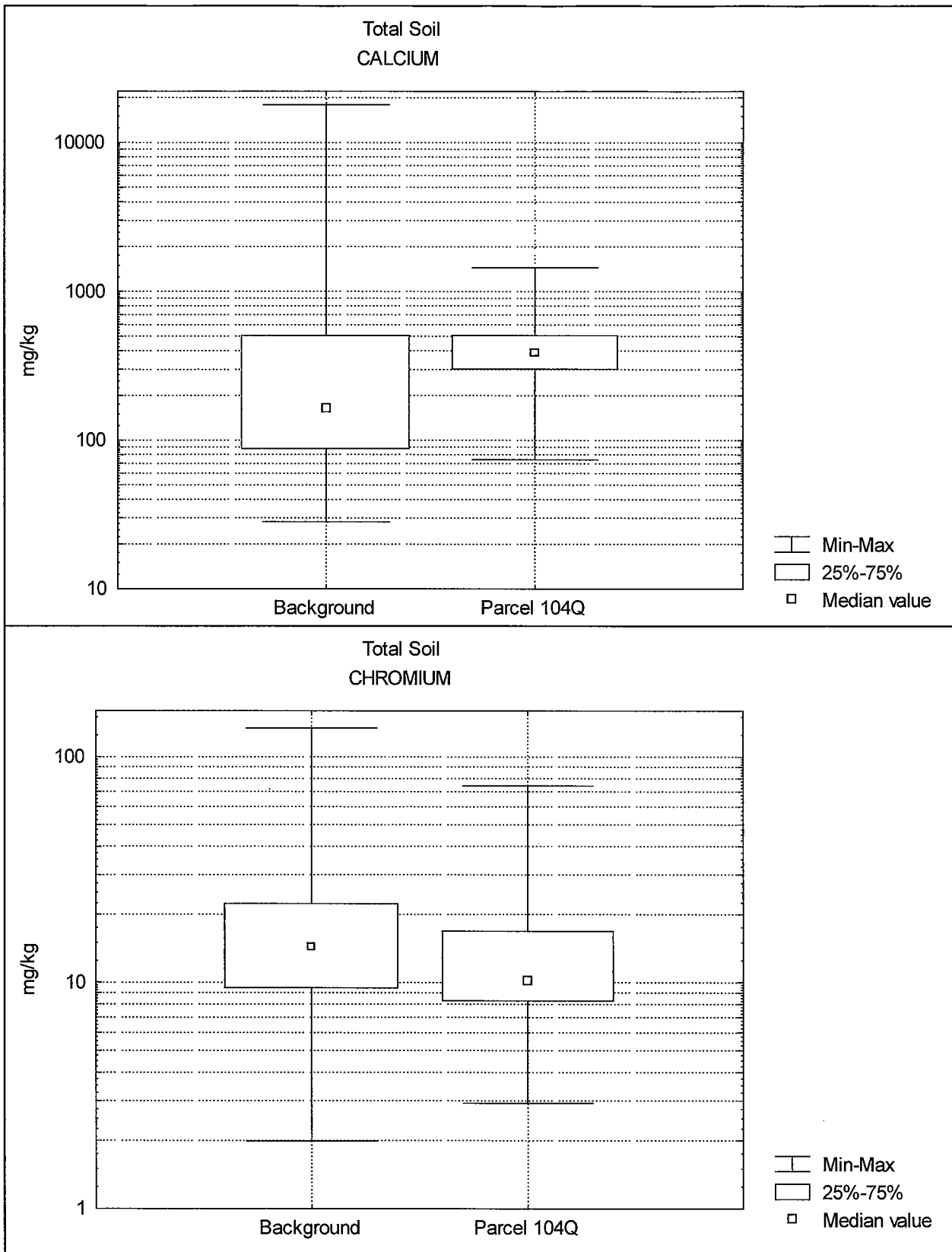


Figure 1-7

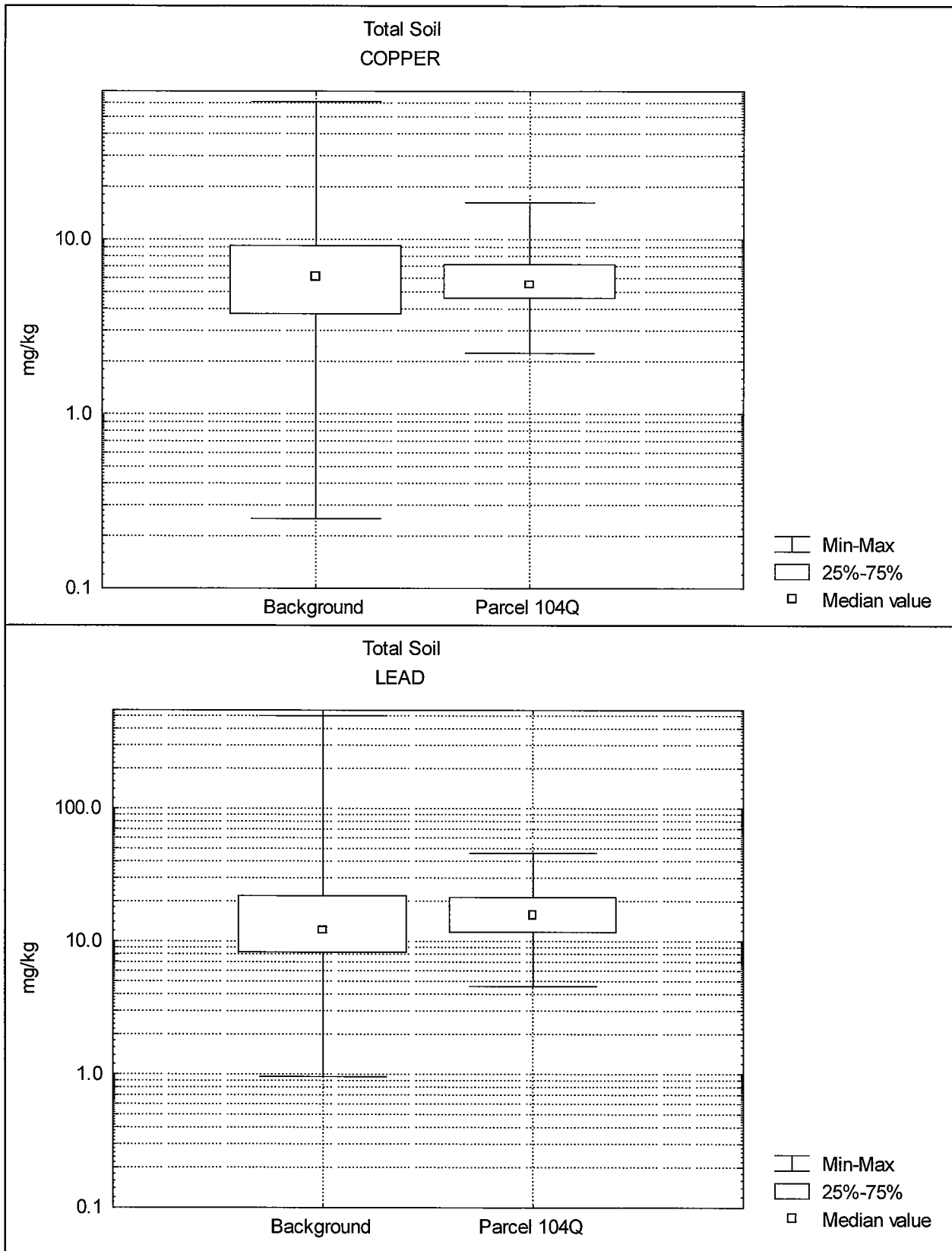


Figure 1-8

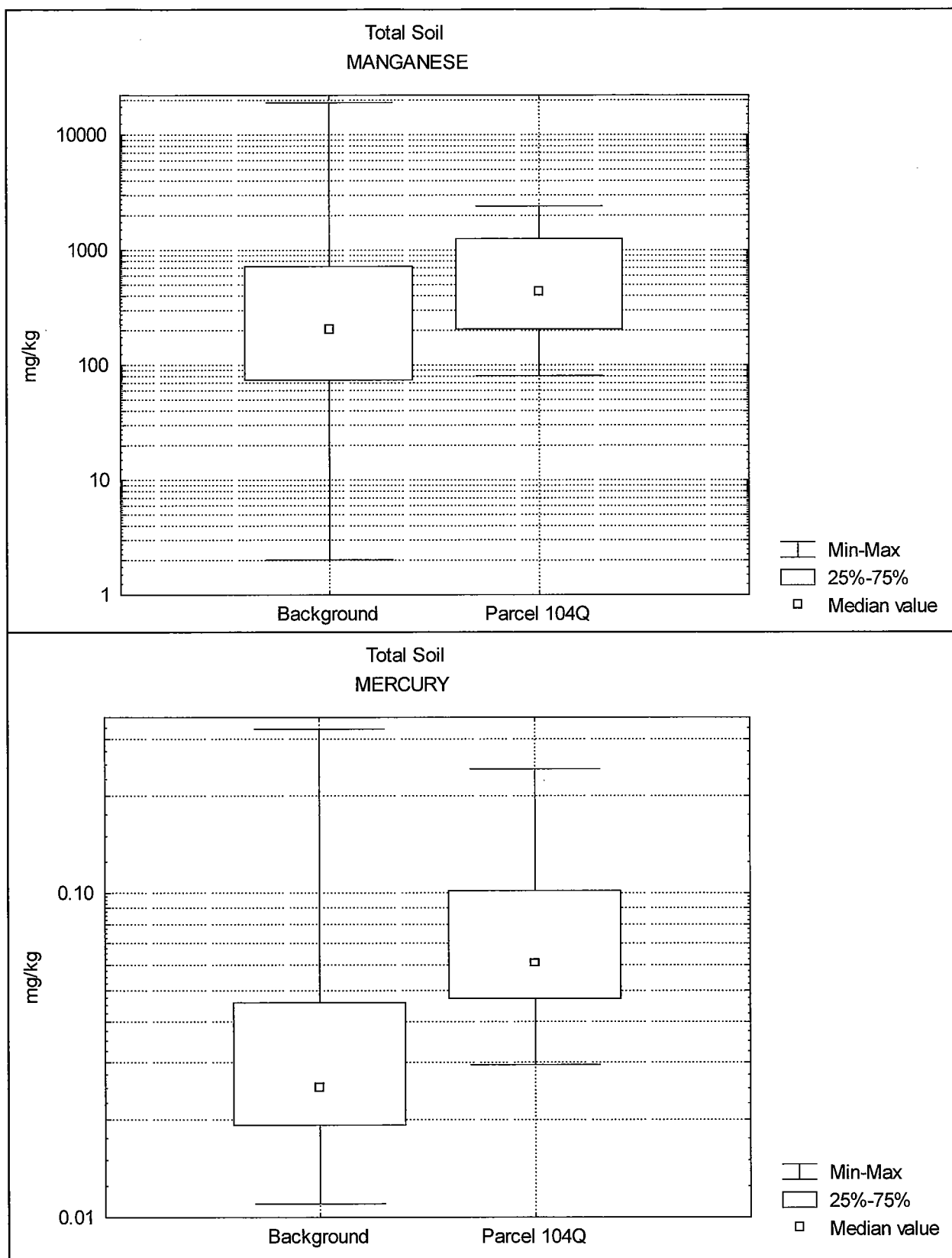
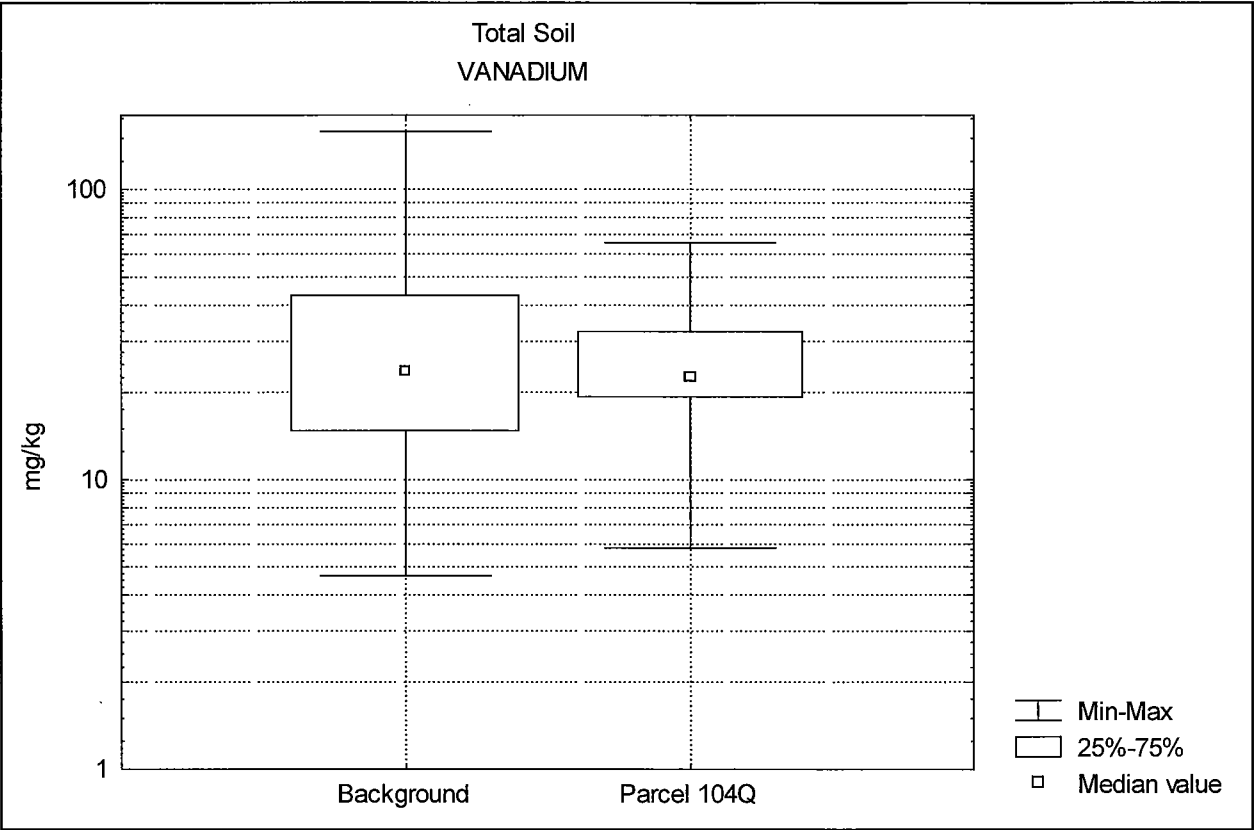


Figure 1-9



GEOCHEMICAL

Geochemical Evaluation of Metals in Soil at the Former Rifle/Machine Gun Range, Parcel 104Q Fort McClellan, Alabama

1.0 Introduction

This report provides the results of a geochemical evaluation of inorganic constituents in soil and groundwater samples from the Former Rifle/Machine Gun Range, Parcel 104(Q), Fort McClellan, Calhoun County, Alabama. Eight elements in the site soil data set failed statistical comparison to background. A geochemical evaluation was performed to determine if the elevated concentrations are naturally occurring or if they contain a component of contamination.

Site samples included in the evaluation consist of 22 surface soil samples (obtained from depths of 0 to 1 foot below ground surface [bgs]) and 22 subsurface soil samples (various depths ranging from 1 to 4 feet bgs) collected in April and June 2002. All of the site samples were analyzed for the full list of 23 target analyte list (TAL) metals. Installation-wide background data for TAL metals in soil are provided in the background study report (Science Applications International Corporation, 1998) and are used in the following evaluation.

2.0 Geochemical Evaluation Methodology

Naturally occurring trace element concentrations in environmental media commonly exceed regulatory screening criteria. Trace element distributions in uncontaminated soil tend to have very large ranges (two to three orders of magnitude are not uncommon), and are highly right-skewed, resembling lognormal distributions. These trace elements are naturally associated with specific soil-forming minerals, and the preferential enrichment of a sample with these minerals will result in elevated trace element concentrations. It is thus important to identify these naturally high concentrations and distinguish them from potential contamination.

If an analyte fails statistical comparison to background as described in the “Statistical Comparison of Site and Background Data for the Former Rifle/Machine Gun Range, Parcel 104(Q),” then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The importance of geochemical evaluations in distinguishing between site and background data sets has been recognized in the industry (U.S. Environmental Protection Agency, 1995; Barclift, *et al.*, 2000; U.S. Navy, 2002; Myers and Thorbjornsen, 2004). When properly evaluated, geochemistry can provide mechanistic explanations for apparently high, yet naturally occurring, constituents. Anomalous samples that may represent

contamination can also be readily distinguished from uncontaminated samples. This section describes the geochemical evaluation techniques that were employed in the site-to-background comparisons for Parcel 104(Q).

It should be noted that the geochemical evaluations rely in part on professional judgment and qualitative assessment is a necessary part of the process. Samples that plot off the linear trend on a correlation plot are certainly suspect, but because all uncertainty cannot be eliminated from the evaluation, such plots cannot be construed as definitive proof of contamination. However, anomalous samples should be flagged as suspect and their results used as a basis for further investigation, risk assessment, or remediation, as appropriate. The combination of statistical evaluations (Tiers 1 and 2) and geochemical evaluation (Tier 3) as presented in this appendix is effective in reducing the occurrences of decision errors relative to consideration of statistics or geochemistry alone.

Soil and Sediment. The geochemical evaluation is based on the natural associations of trace elements with specific minerals in the soil or sediment matrix. As an example, arsenic in most uncontaminated oxic soils is almost exclusively associated with iron oxide minerals (Bowell, 1994; Schiff and Weisberg, 1997). (The term “iron oxide” is used here to include oxides, hydroxides, oxyhydroxides, and hydrous oxides of iron.) This association of arsenic with iron oxides is a result of the adsorptive behavior of this particular trace metal in an oxic soil environment. Arsenic is present in oxic soil pore fluid as negatively charged oxyanions (HAsO_4^- , $\text{H}_2\text{AsO}_4^{2-}$) (Brookins, 1988). These anions have strong affinities to adsorb on the surfaces of iron oxides, which maintain a strong positive surface charge (Electric Power Research Institute, 1986). If a soil sample has a high percentage of iron oxides, then it is expected to have a proportionally higher concentration of arsenic.

The absolute concentrations of arsenic and iron can vary by several orders of magnitude at a site, but the arsenic/iron ratios in the samples are usually quite constant as long as no contamination is present (Daskalakis and O'Connor, 1995). If a sample has some naturally occurring arsenic plus additional arsenic from an herbicide or some other source, then it will have an anomalously high ratio relative to the other uncontaminated samples. These ratios thus serve as a powerful technique for identifying contaminated samples.

The evaluation includes the generation of plots in which detected arsenic concentrations in a set of samples are plotted on the y-axis, and the corresponding detected iron concentrations are plotted on the x-axis. The slope of a best-fit line through the samples is equal to the average

arsenic/iron background ratio. If the samples with the highest arsenic concentrations plot on the same linear trend as the other samples, then it is most probable that the elevated concentrations are natural, and are caused by the preferential enrichment of iron oxides in those samples. If the site samples with elevated arsenic concentrations plot above the trend displayed by the uncontaminated samples, then there is evidence that those samples have an excess contribution of arsenic, and contamination may be indicated.

Each trace element is associated with one or more minerals in the soil matrix. Vanadium and selenium, along with arsenic, form anionic species in solution and are associated with iron oxides, which maintain a positive surface charge. Divalent metals such as barium, cadmium, lead, and zinc tend to form cationic species in solution and are attracted to clay mineral surfaces, which maintain a negative surface charge. These trace elements would be evaluated against aluminum, which is a major component of clay minerals. Manganese oxides also have an affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001). These trace elements would be evaluated against manganese.

3.0 Results of the Geochemical Evaluation for Multiple Elements in Soil

This section presents the results of the geochemical evaluation of aluminum, barium, beryllium, calcium, lead, manganese, mercury, and nickel in soil samples from Parcel 104(Q). Correlation plots are provided in Attachment 1.

Aluminum

Aluminum is the most abundant element analyzed in the site soil samples, with a mean concentration of 15,926 mg/kg (1.6 weight percent). Aluminum is a primary component of common soil-forming minerals such as clays, feldspars, and micas. Aluminum also substitutes for ferric iron in iron oxide minerals, and can adsorb on iron oxide surfaces (Cornell and Schwertmann, 2003). Iron is the second-most abundant element analyzed in the site soil samples, and is mostly present as iron oxides, which are common soil-forming minerals. Clays and iron oxides tend to exist as very fine particles, so both aluminum and iron are enriched in samples with finer grain sizes. The site soil boring logs note that clay and silt are the predominant soil types in many of the sampled intervals, which indicates that the site samples contain a high percentage of fine-grained material.

A plot of aluminum versus iron concentrations provides a qualitative indicator of the relative abundance of clay and iron oxide minerals in site soil (Figure 1). Site surface soil samples are represented by open triangles, site subsurface soil samples by filled triangles, and background soil samples by filled circles. For both soil intervals, the site samples exhibit slightly higher aluminum concentrations than most of the background samples and lie on or slightly above the

general background trend (Figure 1). However, the site samples form a linear trend with a positive slope, indicating that the Al/Fe ratios in the site samples are relatively constant. These observations suggest that the site samples are enriched in clays and other aluminum-bearing minerals relative to the background samples, and that the aluminum has a natural source. It is important to note that clays and iron oxides adsorb specific trace elements (as discussed in Section 2.0), so samples that plot on the upper end of the trend in Figure 1 are expected to contain proportionally higher concentrations of trace elements.

Conclusion

Aluminum detected in the site soil samples is naturally occurring.

Barium

Manganese oxides have an affinity to adsorb divalent cations such as barium and cobalt (Kabata-Pendias, 2001). If a soil sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements. The site and background samples form a collinear trend in a plot of barium versus manganese ($R^2 = 0.86$ and 0.63 for the surface and subsurface intervals) (Figure 2). The site samples with the highest barium concentrations contain proportionally higher manganese concentrations and lie on the trend established by the other samples. These observations indicate that barium in the site samples is associated with manganese oxides at a relatively constant ratio, and is natural.

Conclusion

Barium detected in the site soil samples is naturally occurring.

Beryllium

The site and background samples form a common, generally linear trend in a plot of beryllium versus manganese (Figure 3). The site samples with high beryllium concentrations also have high manganese, and lie on the trend established by the other samples. These observations indicate that beryllium in the site samples is associated with manganese oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Beryllium detected in the site soil samples is naturally occurring.

Calcium

Calcium and magnesium have similar chemical properties, and magnesium often substitutes for calcium in minerals. A plot of calcium versus magnesium is provided in Figure 4. The site and background samples form a generally linear trend with a positive slope. The site samples with the highest calcium concentrations also contain proportionally higher magnesium, and lie on the linear trend. This indicates a natural source for the elevated calcium in the site samples.

Conclusion

Calcium detected in the site soil samples is naturally occurring.

Lead

Manganese oxides in soil have a strong affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001). Samples that contain a high percentage of manganese oxides will contain elevated manganese concentrations and proportionally higher lead. A common linear trend with a positive slope is observed for the site and background samples in a plot of lead versus manganese (Figure 5). The site samples with the highest lead also contain proportionally higher manganese, and lie on the linear trend. Lead in the site samples is associated with manganese oxides at a relatively constant ratio, and is natural.

Conclusion

Lead detected in the site soil samples is naturally occurring.

Manganese

As discussed previously, manganese oxides are common in soil and have an affinity to adsorb specific trace elements such as barium, cobalt, and lead. A positive correlation is thus expected between manganese and associated trace elements in uncontaminated soil samples. The positive correlations observed for barium vs. manganese and lead vs. manganese, and the absence of outliers plotting off the linear trends on the correlation plots, indicate a natural source for these three elements (Figures 2 and 5).

Conclusion

Manganese in the site soil samples is naturally occurring.

Mercury

Mercury concentrations in soil are commonly controlled through organic complex formation (Kabata-Pendias, 2001), so weak correlations between mercury and iron or mercury and aluminum are often observed, even in uncontaminated soil samples. The site and background samples form a generally linear trend with a positive slope in a plot of mercury versus aluminum (Figure 6). The site samples with the highest mercury concentrations also have high aluminum concentrations, and lie on this trend. Mercury in the site samples is associated with clays at ratios consistent with those of the background samples, and is natural.

Conclusion

Mercury detected in the site soil samples is naturally occurring.

Nickel

Nickel has an affinity to sorb on clays (Kabata-Pendias, 2001), so a positive correlation between nickel and aluminum would be expected for uncontaminated samples. A plot of nickel versus aluminum reveals a generally linear trend with a positive slope for most of the background samples (Figure 7). The site samples are strongly linear ($R^2 = 0.83$ and 0.65 for the surface and subsurface intervals) and lie on the background trend. These observations indicate that nickel in the site samples is associated with clays at a relatively constant ratio, and is natural.

Conclusion

Nickel detected in the site soil samples is naturally occurring.

4.0 Summary

Aluminum, barium, beryllium, calcium, lead, manganese, mercury, and nickel in the Parcel 104(Q) soil data set failed statistical comparison to background. Geochemical evaluation indicates that detected concentrations of these elements in the site soil samples are naturally occurring.

5.0 References

- Barclift, D., J. Heath, and A. Drucker, 2000, "Focus on Environmental Background Data Analysis," *Soil Sediment & Groundwater*, August/September, pp. 10-17.
- Bowell, R. J., 1994, "Sorption of Arsenic by Iron Oxides and Oxyhydroxides in Soils," *Applied Geochemistry*, Vol. 9, pp. 279-286.
- Brookins, D. G., 1988, *Eh-pH Diagrams for Geochemistry*, Springer-Verlag.
- Cornell, R. M. and U. Schwertmann, 2003, *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, Second Edition, Wiley-VCH, Weinheim.
- Daskalakis, K. D. and T. P. O'Connor, 1995, "Normalization and Elemental Sediment Contamination in the Coastal United States," *Environmental Science & Technology*, Vol. 29, No. 2, pp. 470-477.
- Electric Power Research Institute, 1986, *Speciation of Selenium and Arsenic in Natural Waters and Sediments, Volume 2: Arsenic Speciation*, EPRI EA-4641, Palo Alto, California.
- Kabata-Pendias, A., 2001, *Trace Elements in Soils and Plants*, Third Edition, CRC Press.
- Myers, J. and K. Thorbjornsen, 2004, "Identifying Metals Contamination in Soil: A Geochemical Approach," *Soil & Sediment Contamination: an International Journal*, Vol. 13, No. 1 (in press).
- Science Applications International Corporation, 1998, *Final Background Metals Survey Report, Fort McClellan, Anniston, Alabama*, July.
- Schiff, K. and S. B. Weisberg, 1997, "Iron as a Reference Element for Determining Trace Metal Enrichment in California Coastal Shelf Sediments," in: S. Weisberg, C. Francisco, and D. Hallock, (eds.), *Southern California Coastal Water Research Project Annual Report 1995-96*, pp. 68-78.
- U.S. Environmental Protection Agency, 1995, *Determination of Background Concentrations of Inorganics in Soils and Sediments at Hazardous Waste Sites*, Office of Research and Development, EPA/540/S-96/500, December.

U.S. Navy, 2002, ***Guidance for Environmental Background Analysis, Volume 1: Soil***, NFESC User's Guide UG-2049-ENV, Naval Facilities Engineering Command, Washington, D.C., April.

ATTACHMENT 1

